EPOXY-SILOXANE LOW VISCOSITY PRE-POLYMER FOR NANOIMPRINT PROCESS

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Nanoimprint lithography technologies (NIL), introduced by Chou et al. in 1995 [1], may be used to overcome the feature size limitation encountered in classical photolithography while remaining more economical than lithographies based on electron, ion beam, x-ray, and scanning probe tips. In the approach involving hot-embossing of a thermoplastic resist layer, a sub-10nm [2] resolution has been achieved, but difficulties, due to polymer flow, have also been identified with the replication of large patterns [3], the use of negative moulds (with a large protruding surface) [4], and the minimization of residual thickness. However, owing to the high viscosity of the thermoplastic resist, even well above glass temperature (T_g), high pressures between 50 bar and 100 bar [5] are needed. These conditions increase the risk of deformation or damage to flimsy substrates, and they may affect predefined structures in a multilevel lithography process thus becoming detrimental to potential applications. Alternative to hot-embossing: a low pressure, moderate temperature imprint process is presented, based on moulding low viscosity prepolymer materials. The benefits of this type of prepolymer will be reported.

The imprinted polymer pattern can be used as a mask for etching, for a lift-off process or directly if its properties are suitable for the application desired. Thus, the polymer properties must match a number of requirements. The viscosity of the pre-polymer must be as low as possible. The polymer must be rigid to avoid deformation of the pattern and exhibit a good adhesion on different substrates (silicon, silica, GaAs, organic layers). The chemical structure of the polymer must allow for wet etching in organic or aqueous solution, for polymer elimination and lift off. This polymer must also be resistant to reactive ion etching (RIE). For accurate moulding, we designed a solution based on the siloxane structure crosslinked via epoxy-amine chemistry. With this system, the polymer properties can easily be modified by adjusting the amine formulation which enables this material to be engineered to optimise performances. Chemical formulation of pre-polymer used in this study are given in **Figure 1**. The siloxane chain: bis(dimethylsiloxane)epoxypropoxypropyl terminated (DMS-DGE), is functionalised with epoxy groups. This molecule is polymerised with diamine: 1.3-bis(aminomethyl)cyclohexane (BAC) or 1,3-bis(aminomethyl)benzene (BAB). All compounds are liquids and the viscosity of each component is less than 9 mPa.s at 20°C.

The silicon moulds were realised by electron beam lithography with a 200 keV electron microscope and dry etching. The size of the moulds was limited to 4 mm x 4 mm by the e-beam system. A pre-polymer drop was laid on the mould pre-heated 2 min at curing temperature to prevent liquid demixing. Both surfaces were brought into contact and pressed for 4 hours at 100°C or 2 hours 30 min at 120°C. Curing temperature and time may be further reduced by using a suitable catalyst. The pressure in these experiments was 15 bars as the lower pressure correctly controlled in our experimental system.

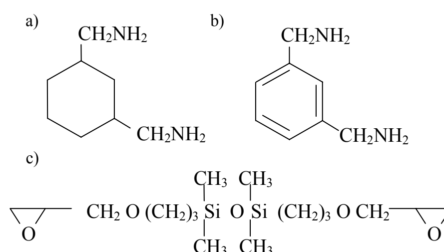

Figure 1 : Formulation of the pre-polymer used in this study a) 1.3-bis(aminomethyl)cyclohexane (BAC) b) 1,3-bis(aminomethyl)benzene (BAB) c) bis(dimethylsiloxane)epoxypropoxypropyl terminated (DMS-DGE).

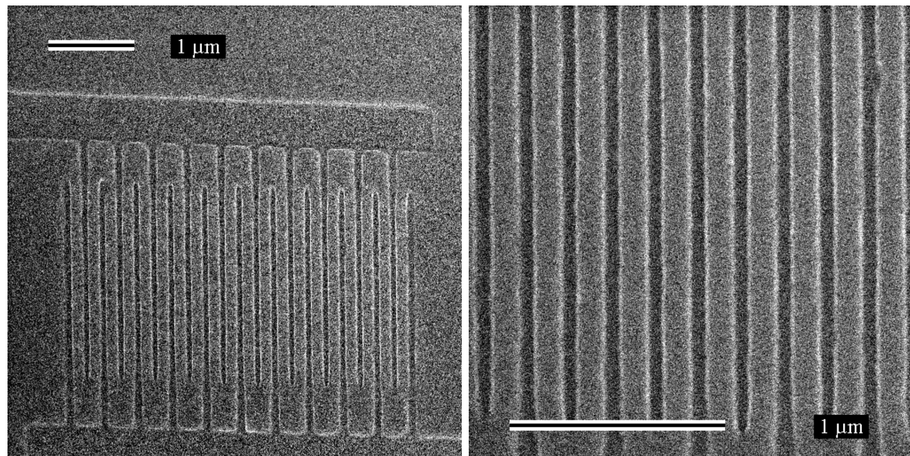

Figure 2 : 60 nm interdigited lines with a 200 nm period. On the right, magnified printed lines shows the good definition of edges

As an example of replicated pattern, **Figure 2** shows 60 nm interdigited lines with a 200 nm period, pattern height being 80 nm. Imprinting smaller and denser patterns (50 nm with a period of 150 nm) leads to line deformation with a two-by-two collapse. This limitation of definition is caused by pattern deformation due to the elastomer characteristic of the epoxy-siloxane resist. To improve resolution T_g or Young modulus of the polymer below the T_g has to be increased by adjusting formulation. The residual thickness obtained when using negative master (with a large protruding surface) is less than 20 nm. This low residual thickness will be taken advantage of for lift-off and for the dimensional control of the features produced. A master containing 60 nm interdigited electrodes and 100 µm x 100 µm adjacent connecting pads has been successfully imprinted without optimisation of the material and procedure process. Furthermore, the same process can be applied to positive and negative master, demonstrating that material transport problems are not restricting the moulding process when using very low viscosity material.

The patterned polymer layer thus obtained can be subsequently used as a mask for etching. An etching selectivity of two compared to silicon has been obtained using RIE with SF_6/O_2 gas mixture. Patterns have also been transferred by lift-off of a 20 nm thick chromium layer, the polymer being dissolved with a sulphuric acid solution in deionized water. To lift off the metal after imprinting with a negative master, the residual layer had to be etched. But using a positive master (with a small bulging surface), lift-off has been possible without etching.

A new type of pre-polymer has been used as a thermocurable resist for low pressure, moderate temperature imprint lithography process. It has been shown that very thin residual layer can be obtained, allowing transfer process without etching of the base layer when positive moulds are used. Micrometer and nanometre scaled patterns can be obtained simultaneously with a very good thickness contrast in the case of positive and negative mould. The imprinted structures are transferred onto silicon using conventional RIE or lift-off process. By adjusting the pre-polymer formulation, the material properties could be further modified to meet specific requirements for various applications : better resolution, and higher etching resistance.

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